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## **An environmentally benign and cost-effective synthesis of Aminoferrocene and Aminoruthenocene**

Leonidova, Anna ; Joshi, Tanmaya ; Nipkow, David ; Frei, Angelo ; Penner, Johanna-Elena ;  
Konatschnig, Sandro ; Patra, Malay ; Gasser, Gilles

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# An Environmentally Benign and Cost-Effective Synthesis of Aminoferrocene and Aminoruthenocene

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## **Abstract**

An improved synthesis of aminoferrocene has been carried out adhering with the basic green chemistry guidelines. Amination from aqueous  $\text{NH}_3$  as nitrogen source, with inexpensive  $\text{CuI/Fe}_2\text{O}_3$  couple as co-catalyst in ethanolic solution makes the process environmentally attractive as well as a viable alternative for all practical purposes. This procedure has also been applied to prepare aminoruthenocene, being reported for the first time.

## Introduction

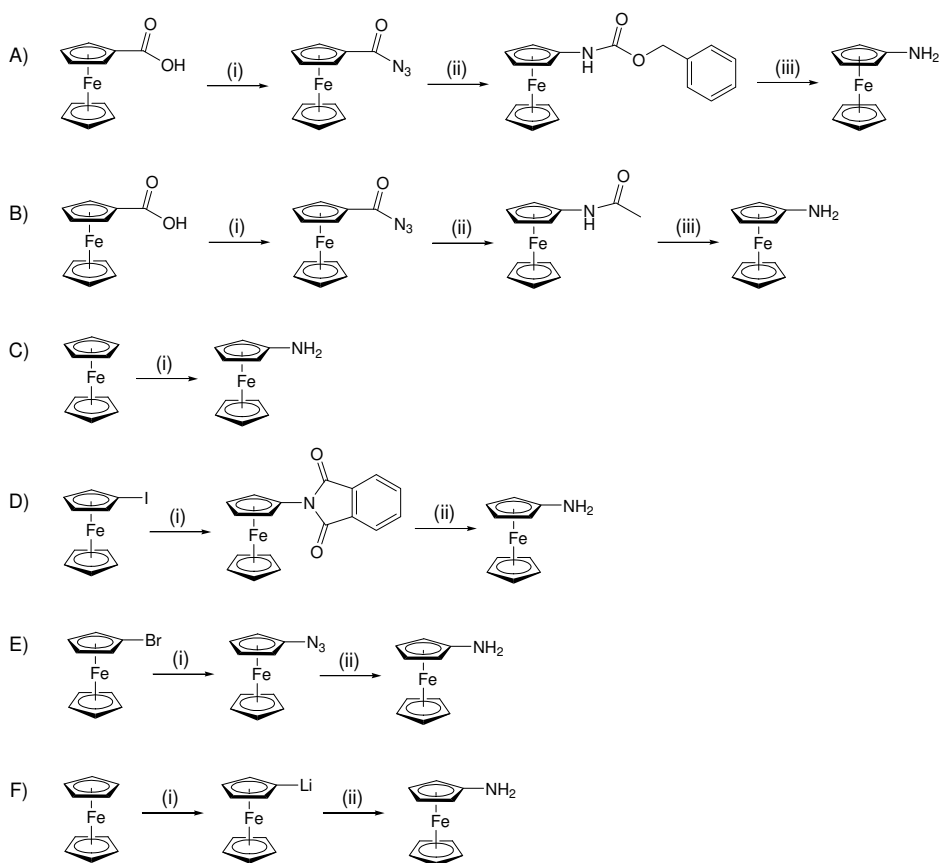
As surprising as it can be, very simple and routinely used aminocyclopentadienyl organometallic derivatives are either not commercially available or extremely expensive. For example, 1g of aminoferrocene, which can be considered as the simplest amino-containing organometallic complex, costs more than 330 Euro!<sup>1</sup> This, we believe, is due to a dearth of industrially scalable procedures that meet demands for producing such a compound in a cost-effective manner. As such, over the last sixty years, several synthetic routes have been developed for laboratory preparation of aminoferrocene. To highlight a few relevant methods, historically, the first synthesis of aminoferrocene was reported by Arimoto *et al.* in 1955.<sup>2</sup> In this procedure, ferrocene carboxylic acid was first reacted with  $\text{PCl}_5$  in benzene and then with  $\text{NaN}_3$  in acetone to form ferrocenoyl azide (reaction A in Scheme 1). The desired aminoferrocene was finally obtained via Curtius rearrangement and subsequent removal of the benzyl formate group. In 2002, Butler *et al.* reported a further improvement to this synthesis where use of milder conditions afforded a better yield from a similar synthetic pathway.<sup>3</sup> Earlier to this, in 1983, Herberhold *et al.* proposed a slightly modified strategy involving the preparation of *N*-ferrocenylamide, which can be transformed to aminoferrocene under basic conditions (reaction B in Scheme 1).<sup>4</sup> Another approach was proposed by Knox *et al.* in 1990. It involved first *n*-butyllithium mediated lithiation of ferrocene and then the reaction of the monolithiated ferrocene with *O*-benzylhydroxylamine (reaction C in Scheme 1). However, the post acid treatment yielded only a relatively small amount of the desired aminoferrocene.<sup>5</sup> Bildstein *et al.* reported in 1999 another optimized and high-yielding synthetic pathway involving the sequence ferrocene - solid monolithioferrocene – iodoferrocene – ferrocenyl phthalimide – aminoferrocene based on the initial work from Sato, Nesmeyanov and co-workers.<sup>6-8</sup> This procedure was later slightly

modified by Heinze *et al.*<sup>9</sup> More specifically, in this method, iodoferrocene, which can be obtained from readily available ferrocene, is used as the starting material. Coupling of iodoferrocene with copper phthalimide gave ferrocenyl phthalimide, which was converted to aminoferrocene via Gabriel synthesis (reaction D in Scheme 1). Another widely utilized method for making aminoferrocene involves the preparation of azidoferrocene from bromoferrocene and its subsequent reduction with  $\text{LiAlH}_4$ <sup>10</sup> or by hydrogenation (reaction E in Scheme 1).<sup>11</sup> Even though this hydrogenation approach has only been used to synthesize 1,1'-diaminoferrocene from 1,1'-dibromoferrocene via 1,1'-diazidiferrocene,<sup>11</sup> it can be anticipated that it would also work for the monosubstituted ferrocene. However, the procedure presents a major drawback as azidoferrocene can potentially be explosive – 1,1'-diazidiferrocene is prone to explosion if heated rapidly above 56 °C.<sup>11</sup> In 2001, van Leusen *et al.* proposed a two-step strategy involving first the deprotonation of ferrocene and then the use of  $\alpha$ -azidostyrene (reaction F in Scheme 1).<sup>12</sup> However, the latter is not commercially available and the preparation requires a three-step synthetic route.

Hence, to summarize, the best available procedures for aminoferrocene synthesis require either several synthetically challenging steps, are low-yielding or involve the preparation of potentially explosive intermediates. Considering the potential of ferrocene in a multitude of research areas,<sup>13</sup> there is definitively a need for a simple and efficient synthetic pathway for preparing aminoferrocene and, more generally, for organometallic aminocyclopentadienyl derivatives. To emphasize the importance of such small amino-functionalized ferrocenyl compounds, it has to be reminded that they have already been used, for example, as building blocks for the preparation of ferrocenyl peptide bioconjugates as well as aminoferrocene based prodrugs.<sup>14-20</sup> One such conjugate showed potential for the electrochemical sensing of chemical warfare agent mimics.<sup>19-</sup>

<sup>20</sup> Over the recent years, such small organometallic constructs have also been used as inserts for parent organic drugs to prepare novel organometallic-based antiparasitic and anticancer drug candidates.<sup>21-22</sup>

Herein, we report, to the best of our knowledge, the most environmentally-friendly and economically attractive synthesis of aminoferrocene and aminoruthenocene from corresponding mono-substituted iodo precursors using aqueous ammonia and an iron/copper co-catalyst system (Scheme 2).



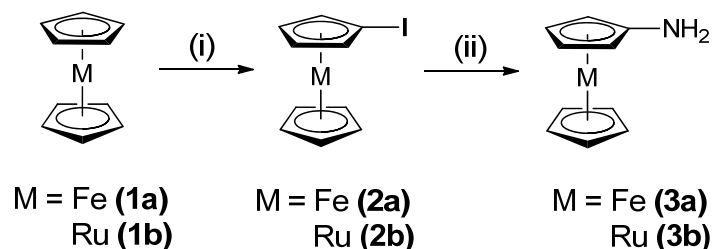
**Scheme 1.** Non-exhaustive list of synthetic procedures to prepare aminoferrocene. **A)** Synthesis proposed by Arimoto *et al.*<sup>2</sup> (i) 1.  $\text{PCl}_5$ , benzene; 2.  $\text{NaN}_3$ , Acetone; (ii) Phenylmethanol; (iii)  $\text{NaOH}$  (10 %); **B)** Synthesis proposed by Herberhold *et al.*<sup>4</sup> (i) 1.  $\text{PCl}_5$ , benzene; 2.  $\text{NaN}_3$ , Acetone; (ii) Acetic anhydride; (iii)  $\text{KOH}$  (10 %); **C)** Synthesis proposed by Knox *et al.*<sup>5</sup> (i) 1. *n*- $\text{BuLi}$ ,  $\text{Et}_2\text{O}$ ; 2. benzylhydroxylamine; 3.  $\text{HCl}/\text{H}_2\text{O}$ ; **D)** Synthesis proposed by Heinze *et al.*<sup>9</sup> (i)

Copper phthalimide; (ii)  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ ; **E**) Synthesis proposed by Arnold *et al.*<sup>11</sup> (i)  $\text{NaN}_3$ ,  $\text{CuCl}$ ,  $\text{EtOH}/\text{H}_2\text{O}$ ; (ii)  $\text{H}_2$ ,  $\text{Pd}/\text{C}$  (5 %  $\text{Pd}$ ),  $\text{MeOH}$ ; **F**) Synthesis proposed by van Leusen *et al.*<sup>12</sup> (i) *t*- $\text{BuLi}$ ,  $\text{THF}$ ; (ii) 1.  $\alpha$ -azidostyrene; 2.  $\text{HCl}/\text{H}_2\text{O}$ .

## Results and Discussion

As described in Scheme 2, the synthetic strategy that we report herein for aminoferrocene synthesis involves the preparation of iodoferrocene from ferrocene and its corresponding amination using aqueous ammonia. For this, the iodoferrocene precursor was easily prepared following the recently reported procedure from Goeltz and Kubiak.<sup>23</sup> Inspired by the recent report by Wu and Darcel, which describes a ligand-free iron/copper-co-catalyzed amination of aryl iodides with aqueous ammonia,<sup>24</sup> we could successfully optimize the reaction conditions to isolate aminoferrocene in 65 % yield after purification. To the best of our knowledge, this is the simplest route reported so far for preparing aminoferrocene. Furthermore, use of cheap co-catalysts (iron and copper salts), ethanol as solvent and aqueous ammonia for nitrogen source, makes the procedure environmentally-friendly as well as economically attractive, even for industrial purposes.<sup>24</sup> Of note, we also assessed the possibility of employing similar copper(I) iodide mediated Ullmann-type coupling as reported by Bolm and co-workers for the preparation of nitrogen-substituted ferrocenes.<sup>25</sup> While aminoferrocene could still be obtained following this approach, addition of co-catalyst, iron(III) oxide, however, results in a 2-fold increase in the reaction yield. A similar improvement in reaction yields was also observed by Wu and Darcel for amination of aryl iodides.<sup>24</sup> The iron/copper co-catalyst system allowed us to use ethanol/water as solvent instead of dimethylsulfoxide (DMSO) hence avoiding the use of Schlenk techniques (quite frequently employed in synthetic organometallic chemistry), and shortening the reaction time from 16 to 6 hours in comparison with the conditions originally reported by Bolm and co-

workers. Furthermore, in absence of any sodium hydroxide, only a slight decrease in reaction yield (ca. 10 %) was observed for a 100-fold excess of ammonia solution being used.



Scheme 2. Aminoferrocene and Aminoruthenocene synthesis proposed by our group. (i) *t*-BuLi, I<sub>2</sub>, THF,<sup>23, 26</sup> (ii) NH<sub>3</sub> (aq), CuI (10 mol %), Fe<sub>2</sub>O<sub>3</sub> (10 mol %), NaOH, EtOH, 90 °C.

Encouraged by the excellent results obtained for aminoferrocene, taking a step further, we also attempted the preparation of its heavier homologue, aminoruthenocene, via a similar pathway. As expected, the desired product was successfully isolated, in 60 % yield, with no further chromatographic purification. The identity of the product was established by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, IR spectroscopy, ESI-MS and high resolution mass spectrometry (HRMS). The <sup>1</sup>H NMR spectra showed multiplets between 4.10-4.40 ppm, characteristically assigned to the mono-substituted ruthenocene, a broad signal at 3.07 ppm ascribable to the –NH<sub>2</sub> group, and signals for the corresponding carbons in the <sup>13</sup>C NMR spectra. Signal at *m/z* = 248.0 for the corresponding [M+H]<sup>+</sup> ion observed in ESI-MS further confirmed the formation of the desired aminoruthenocene product.

## Conclusion

In summary, in this work, we present a remarkable improvement over the methodologies available for preparation of aminoferrocene. The applied synthetic route is, to the best of our



knowledge, the most direct pathway reported thus far in the literature. Importantly, the use of inexpensive CuI/Fe<sub>2</sub>O<sub>3</sub> couple as co-catalysts and of NH<sub>3(aq)</sub>/EtOH as reaction medium make this procedure an environmentally-friendly and cost-effective route. Moreover, using aminoruthenocene as an example, we could successfully show that scope of this amination strategy can potentially be extended to prepare other small organometallic building blocks, further adding to its advantage over existing protocols.

### Experimental section.

**Materials.** All chemicals were of reagent grade quality or better, obtained from commercial suppliers and used without further purification. Solvents were used as received or distilled using standard procedures.<sup>27</sup> *Thin layer chromatography (TLC)* was performed using silica gel 60 F-254 (Merck) plates with detection of spots being achieved by exposure UV light. *Column chromatography* was done using Silica gel 60 (0.040-0.063 mm mesh, Merck). Eluent mixtures are expressed as volume to volume (v/v) ratios. Iodoferrocene (**2a**)<sup>23</sup> and iodoruthenocene (**2b**)<sup>26</sup> were synthesised according to literature procedures.

**Instrumentation and methods.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in deuterated solvents on AV2-401 spectrometer, at room temperature. The chemical shifts,  $\delta$ , are reported in ppm (parts per million). The signals from the residual protons of deuterated solvent have been used as an internal reference.<sup>28-29</sup> The abbreviations for the peak multiplicities are as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiplet), and br (broad). *ESI mass spectrometry* was performed using a Bruker Esquire 6000 spectrometer. In the assignment of the mass spectra, the most intense peak is listed. *High-resolution accurate mass spectra* were recorded with Bruker maXis QToF high-resolution mass spectrometer (Bruker Daltonics,

Bremen, Germany). *Infrared spectra* were recorded on Perkin-Elmer FTIR spectrometer fitted with an ATR platform. Peak intensities are given as broad (b), very strong (vs), strong (s), medium (m) and weak (w).

### Synthesis.

**Aminoferrocene (3a):** Iodoferrocene (0.10 g, 0.32 mmol) was dissolved in EtOH (3 mL). Copper iodide (6.0 mg, 0.032 mmol), Fe<sub>2</sub>O<sub>3</sub> (5.0 mg, 0.032 mmol) and NaOH (30 mg, 0.75 mmol) were added to the solution. Aqueous ammonia (13.5 M, 1.5 mL) was added to the resulting red solution and the reaction mixture was heated at 90 °C for 6 hours in a pressure-proof vessel. The reaction mixture was cooled to room temperature and diethyl ether (50 mL) was added. The organic phase was then washed with 1 M aqueous NaOH (3 × 50 mL), dried over anhydrous MgSO<sub>4</sub>, filtered and evaporated to dryness to obtain the crude product, which was purified by silica gel column chromatography (SiO<sub>2</sub>, eluent gradient gradually changed from hexane:EtOAc 1:1 to hexane:EtOAc 1:4) to obtain **3a** as a yellow-orange solid. Yield: 42 mg (65 %). (*R*<sub>f</sub> = 0.38 in hexane:EtOAc 1:4). The analytical data for **3a** matched with that previously reported.<sup>3</sup>

**Aminoruthenocene (3b):** Compound **3b** was prepared following a procedure similar to that described for **3a**, using iodoruthenocene (0.17 g, 0.47 mmol), copper iodide (8.9 mg, 0.047 mmol), Fe<sub>2</sub>O<sub>3</sub> (7.5 mg, 0.047 mmol) and NaOH (47 mg, 1.18 mmol), and aqueous ammonia (13.5 M, 2.1 mL) in EtOH (8 mL). The reaction mixture was cooled to room temperature, diethyl ether (70 mL) was added and the ethereal solution was washed with 10 mM phosphate buffer (pH 7.01) (2 × 25 mL). The organic phase was extracted with water (2 × 15 mL) acidified to pH

3.0 using 1M HCl), freeze-dried to obtain hydrochloride salt of **3b** as a off-white solid. The hydrochloride salt was dissolved in water (10 mL) and the pH of the aqueous solution was adjusted between 7-8 using 1M NaOH. After extraction with dichloromethane (3 × 35 mL), the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure to obtain an analytically pure sample of aminoruthenocene as yellowish black solid.<sup>30</sup> Yield: 69 mg (60 %). Anal. calcd. for C<sub>10</sub>H<sub>12</sub>ClNRu (%): C, 42.48; H, 4.28; N, 4.95. Found: C, 42.66; H, 4.52; N, 4.86. IR (ATR):  $\nu$  3405w (N-H), 3281w, 3087s (C-H), 2925w (C-H), 1494vs, 1408m, 1255s, 1099s, 995s, 799vs cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, THF-d<sub>8</sub>):  $\delta$  4.41-4.40 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 4.38 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.11-4.10 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 3.07 (br s, 2H, -NH<sub>2</sub>) ppm. <sup>13</sup>C NMR (100 MHz, THF-d<sub>8</sub>):  $\delta$  112.2, 70.9, 65.9, 62.1 ppm. MS (ESI<sup>+</sup>):  $m/z$  248.0 [M+H]<sup>+</sup>. HR-ESI mass spectrum (methanol + NaI): found 248.00045; calcd. for [C<sub>10</sub>H<sub>12</sub>NRu]/z 248.00077.

#### ASSOCIATED CONTENT

**Supporting Information.** <sup>1</sup>H and <sup>13</sup>C NMR spectra (Figures S1-S2) and ESI-MS of **3b** (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. # These authors contributed equally.

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30. *Note: Slow decomposition of aminoruthenocene in halogenated solvents was observed in the presence of light. Therefore, as much as possible, the workup procedure should be carried out in absence of light and prolonged suspension of aminoruthenocene in halogenated solvents should also be avoided. To increase lifetime of aminoruthenocene, their storage as hydrochloride salt below -20 °C is recommended.*

TOC:

## **An Environmentally Benign and Cost-Effective Synthesis of Aminoferrocene and Aminoruthenocene**

Adhering with the basic green chemistry guidelines, an environmentally friendly and practically viable alternative synthesis of aminoferrocene and aminoruthenocene has been reported.

